

made for evaluation at various rates and depths of discharge. Both the carbon electrode and the CX1 electrode were used as the counter electrode for this study. Preliminary test results show that the lithium electrode in the EX1 electrolyte has a cycling efficiency of 85 to 87 percent operating with the carbon counter electrode and a better efficiency of about 92 to 94 percent operating with the CX1 counter electrode. The current density of 0.5 to 2 mA/cm² had no significant effect on the cycling efficiency. The cycling efficiency of lithium in the EX2 electrolyte is estimated to be higher than 97 percent.

The development of an all-inorganic, ambient temperature, lithium solid cathode system using the low cost electrolyte will continue to be emphasized during the coming quarters.

The objectives for 1983 are to characterize CX1 cathode and Li anode cycling in the EX2 electrolyte and to establish the performance capability and identify the problem areas using experimental cells.

Recent publications

- 1 W. Bowden, Electrochemical oxidation of polyhedral boron halide anion, *J. Electrochem. Soc.*, 129 (1982) 1249 - 1252.

SULFOLANES AS ELECTROLYTE SOLVENTS FOR RECHARGEABLE LITHIUM BATTERIES

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The purpose of this research is to investigate the possible use of sulfolanes in rechargeable lithium batteries. The critical parameters are the conductivity of sulfolane electrolytes, the stability of these electrolytes, and the ability of the electrolytes to cycle lithium. Tests will be conducted on pure sulfolane electrolytes and on sulfolane blends with ethers.

To date, efforts in the program have been concentrated on the purification of sulfolane (S). In addition, the stability of S to Li (and Na/K) and the electrochemical limits of electrolyte solutions have been investigated. Conductivities of electrolyte solutions in S and S-ether mixtures have been surveyed. A test cell for half-cell Li cycling was developed, and initial cycling experiments were performed.

Sulfolane has commonly been selected for use as a solvent because of its resistance to oxidation. Many purification schemes are tailored for this application. The goal is to develop a purification scheme for the removal of

reducible impurities that offers minimal risk of introducing new impurities. Ideally, this scheme would not be overly labor intensive or require exotic materials or apparatus.

Ultraviolet (UV) spectroscopy was chosen as a guide to the development of a purification scheme. Sulfolane is nearly transparent in the UV spectrum, and this transparency has been used as a criterion for purity in past work. A variety of purification techniques have been explored and a preferred sequence identified. This sequence includes vacuum distillation, treatment with adsorbant, and fractional crystallization. Although it is a relatively lengthy process, it is not labor intensive. Sulfolane thus purified will serve as a feedstock for further reductive and electrochemical purification.

Substituted sulfolanes typically have lower freezing points than S. Thus, 3-methyl sulfolane (f.p. 0 °C) was investigated for use as an electrolytic solvent in Li batteries. It appears to have little or no advantage over S. The commercial solvent appears to contain more impurities than S. The conductivity of its LiAsF₆ solution is less, and its viscosity is nearly equal to that of S at 30 °C. Additionally, the freezing point difference is of secondary importance because electrolyte solutions in sulfolane are liquid at room temperature and sulfolane would most likely be used with a cosolvent in any case. As a result, the investigation has in the past, and will in the future, concentrate on S.

In initial storage tests, S electrolytes were observed to be stable to Li metal for weeks at 70 °C. Pure sulfolane appears less stable to Li metal but shows little or no reaction with Li/Hg. These test results are promising. Further tests of the stability of S await the availability of more highly purified samples of S. Sulfolane reacts rapidly and completely with Na/K alloy, producing a blue, solid product.

Electrolyte solutions in sulfolane have conductivities similar to solutions in 2Me-THF (*i.e.*, 1 M LiAsF₆/0.0027 ohm⁻¹ 30 °C). In blends with relatively polar ethers, synergistic conductivity effects are observed. The type and magnitude of these effects vary with the ether.

Lithium cycling experiments using S electrolytes have begun. A test cell that allows half-cell cycling of Li from thin, Li foil electrodes was developed. In initial work using such a cell, cycling efficiencies greater than 50 percent have been observed.

Purification of S will continue with an emphasis on Li treatment and electrochemical techniques. To supplement UV analysis, additional analytical techniques, including electrochemical analysis, will be investigated.

The stability of S to reduction will be investigated routinely using storage tests at elevated temperatures. However, the investigation will be extended by attempts to reduce S electrochemically. Cathode materials, which are relatively immune to the formation of surface films, will be used. Product identification may be necessary and would be attempted using thin-layer chromatography. This work will be an attempt to reconcile the reactivity of S with Na/K to the apparent lack of reactivity with Li.

The cycling studies of sulfolane electrolytes in Li half-cells will be continued to assess their cycling efficiencies and to gain insight into purification. The cycling will be extended to sulfolane-ether mixtures showing greater conductivity and lower viscosity than sulfolane alone. If acceptable cycling is observed in half-cells, Li/TiS₂ cells will be constructed and cycled.

OVERVIEW OF IRON/AIR BATTERY DEVELOPMENT AT WESTINGHOUSE

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The development of the iron/air system at Westinghouse has concentrated on the bifunctional electrode during the last 2 years. The current program goals are to demonstrate stable performance compatible with a commuter electric vehicle mission with cycle life in excess of 1000 duty cycles. Work in previous years has demonstrated stable performance for the iron electrode at 0.4 A h/g. This level of performance is compatible with the vehicle requirements for this battery system. Additional work to advance this level of performance was deferred to concentrate our efforts on the air electrode.

The research and development program on the air electrode has three basic tasks with a parallel program at Case Western Reserve University (CWRU) complimenting these areas of research. The first task is to advance the performance and life of the current state-of-the-art bifunctional air electrode.

The current electrode system has demonstrated stable performance for greater than 500 cycles over 4000 h of testing. Alternative electrode compositions and electrode processing procedures were evaluated and tested. The results have indicated that the structure of the current air electrode overrides the catalyst used for performance and life. The results of CWRU have substantiated the chemical stability of the state-of-the-art air electrode while also identifying structural deficiencies in the current electrode system. Recent test results of various state-of-the-art electrodes will be discussed.

The second area of research has considered alternative electrode compositional additives for improved performance in the oxygen evolution mode as well as the oxygen reduction mode. Initial characterization of the candidate additives used cyclic voltammetry in conjunction with a floating electrode technique to determine perhydroxyl rate elimination constants. As a result of the screening of possible additives, a new combination of materials has been identified. To date, these new additives have demonstrated nearly